from (10) as we cannot completely exclude the possibility that the chains considered in our calculations were too short for determining the right asymptotic behavior or even that the data themselves were not as reliable as expected at high concentrations. We nevertheless consider that the value reported here for γ does not really conflict with the neutron diffraction data and that the claim, found in the literature, that intra- and intermolecular interaction *exactly* balance each other for the bulk polymer cannot be regarded as well established at the present time.

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Theoretical Determination of Helix–Coil Parameter σ from a Model of Partly Helical Polypeptide Chain

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ABSTRACT: The Zimm and Bragg parameter σ is calculated numerically for poly(L-alanine), polyglycine, and the copolymers of L-alanine and glycine using the molecular theory of s and σ as developed by Go, Go, and Scheraga in a modified formulation. In this formulation, σ is obtained from the partition function of the whole chain in the helix–coil transition region and represents therefore the contributions from the ends of helical and coil sequences and from the interactions between atoms in a coil sequence with those in the neighboring helical sequence. When the parameter σ is calculated numerically from a hard-sphere potential, it appears that steric interactions between atoms in the coil sequence with atoms in the neighboring helical sequence, which have been neglected in previous calculations, contribute significantly to the value of σ. Owing to these interactions the entropy of the coil sequence as well as σ decrease, but the decrease of σ is larger in poly(L-alanine) than in polyglycine, because of the higher flexibility of the monomer in polyglycine. The numerical value of σ for polyglycine compared with that of poly(L-alanine) might be overestimated however by the model presented here due to approximations inherent in the hard-sphere treatment and because only regular helical sequences are considered.

One of the most promising ways of predicting the secondary structure of proteins is the calculation of helical profiles from the partition function of the chain using Zimm and Bragg parameters s and σ for various residues of amino acids.[2] It is therefore of interest to refine the methods of calculation of σ and s.

These parameters can be obtained from the free energies computed with the help of semiempirical potential functions. The enthalpic contribution to σ from helical sequences has been calculated by Brant[3] for poly(L-alanine). A complete molecular theory of s and σ has been developed by Go, Go, and Scheraga.[4] Subsequently, the parameters s and σ for poly(L-alanine) and polyglycine have been computed numerically from this theory.[5,6]

Here we compute σ using this molecular theory in a modified formulation, by deducing σ from a numerically determined partition function for a chain composed of helical as well as coil sequences. Therefore the ends of both the helical and the coil sequences and the interactions between them contribute to σ. In the theory of Go, Go and Scheraga,[5] atoms in the helical sequence are treated to interact at the junction with such atoms in the neighboring coil sequence, whose positions are determined only by the first rotatable dihedral angle in the coil sequence. Interactions are neglected with atoms in the coil sequence separated further from the junctions.

The modified method for the calculation of σ will be presented in section I and will in section III be applied to poly(L-alanine) and to polyglycine and to copolymers of glycine and L-alanine, using a hard-sphere potential.

With this potential it is easy to locate all atoms involved in steric repulsions. Moreover the values of σ computed from a hard-sphere potential are representative of interactions neglected in previous calculations. In particular, the influence of flexibility of glycyl residue on σ will be investigated, by comparing σ for poly(L-alanine) and for polyglycine as well as for sequential copolymers of glycine and L-alanine.

The description of the model representing the partly helical chain is given in section II and the numerical results in section IV. In section V the method of calculation of σ as well as the numerical results are discussed.

I. Method of Calculation of s and σ

Let us consider a partly helical polypeptide chain with a given distribution γ of helical and coil sequences. This distribution contributes to the partition function by a term Z_γ which may be represented formally by the following expression

$$Z_\gamma = u_{i_1} v_{j_1} u_{i_2} v_{j_2} \cdots v_{j_\nu} u_{i_{\nu+1}} = \pi_{(\nu)} [u_{i_k} v_{j_k}] u_{i_{\nu+1}} \quad (1)$$

where u_{i_k} and v_{j_k} arise from coil and helical sequences containing i_k and j_k residues, respectively; k is the number of

the considered sequence in the chain, ν is the total number of helical sequences. A sequence is considered to be helical when at least three adjoining residues have appropriate values of ϕ,ψ angles.

In this particular distribution, there is a total of i residues in the $\nu + 1$ coil sequences and j residues in the helical sequences, so that we have

$$i = \Sigma_{\nu+1} i_k \qquad j = \Sigma_{\nu} j_k \tag{2}$$

Let us rewrite (1) in the following way

$$Z_\gamma = u_0{}^i v_0{}^j \sigma_\gamma{}^\nu = u_0{}^{i+j} s^j \sigma_\gamma{}^\nu \tag{3}$$

where u_0 and v_0 are the contributions to the partition function of a residue in an infinitely long coil and helical sequence, respectively. The parameter s represents the ratio of v_0 to u_0. This equation defines the parameter σ_γ.

The values of u_0 and v_0 can be obtained from expression 3 in ref 2

$$u_0 = \lim_{n\to\infty} u_{n+1}/u_n \qquad v_0 = \lim_{n\to\infty} v_{n+1}/v_n \tag{4}$$

where u_n is the partition function of a chain with n residues in a coil state, given by the following expression

$$u_n = \int_0^{2\pi} d\phi_1 \int_0^{2\pi} d\psi_1 \cdots \int_0^{2\pi} d\phi_n \int_0^{2\pi} d\psi_n \times \exp[-E(\phi_1, \psi_1, \ldots, \phi_n, \psi_n)/RT] \tag{5}$$

In eq 5, ϕ and ψ are the dihedral angles for rotation about N–C$^\alpha$ and C$^\alpha$–C′ bonds, respectively, and $E[\phi_1,\psi_1,\ldots,\phi_n,\psi_n]$ is the conformational energy. Each integration extends from 0 to 2π. A similar expression is obtained for v_n, but in this case integration is limited to a small region of ϕ,ψ multidimensional phase space compatible with the α helical structure.

The contribution to the partition function Z_γ for a given distribution γ of a partly helical polypeptide chain of n residues can be analogously defined by the expression

$$Z_\gamma = \int d\phi_1 \int d\psi_1 \cdots \int d\phi_k \int d\psi_k \cdots \int d\phi_n \int d\psi_n \times \exp[-E(\phi_1, \psi_1, \ldots, \phi_k, \psi_k, \ldots, \phi_n, \psi_n)/RT] \tag{6}$$

where the numbering of the residues must correspond to their position in the polypeptide chain according to a fixed rule. The integration of the angles ϕ_k,ψ_k for a residue in a coil sequence extends from 0 to 2π but for a residue in a helical sequence is limited as in definition of v_n.

Using eq 4, 5, and 6, u, v, and Z can be computed numerically from semiempirical potential functions and an appropriate model of the chain.

We shall assume that σ_γ as defined by eq 3 does not depend significantly on the length and distribution of the coil and helical sequences so that any of the possible distributions can be used for the calculation of σ_γ and the subscript γ can then be omitted. In particular, the simplest possible distribution with one single helical sequence and coil sequences at both ends of the helix can be considered.

The parameter σ as defined by eq 3 takes into account all specific interactions arising from the junctions between helical and coil sequences, as well as from the terminal parts of both the helical and coil sequences. Therefore the definition of σ given here is different from that used by Go, Go, and Scheraga (eq 4 of ref 4), in which atoms in the helical sequence are treated to interact at the junction only with such atoms in the neighboring coil sequence whose positions are determined only by the first rotatable dihedral angle in the coil sequence. It can be seen that eq 3 will be identical with the definition of σ of Go, Go, and Scheraga if (a) a coil sequence u_{i_k} contributes to the partition function by a factor $u_0{}^{i_k}$, (b) only one helical sequence is considered ($\nu = 1$), and if (c) the following condition holds: $\lim_{n\to\infty} (v_{n+1}/v_n) = v_0$.

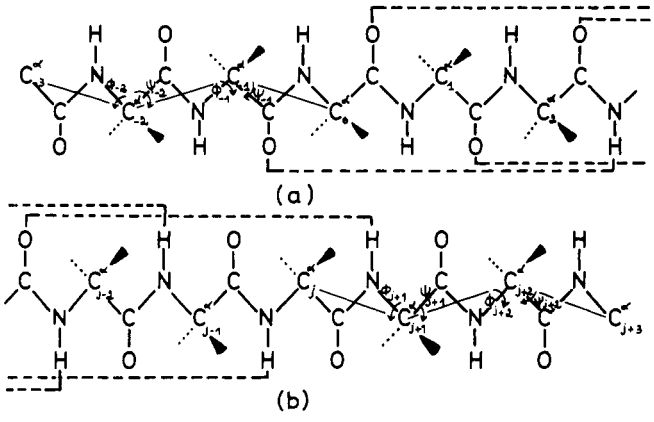

Figure 1. Schematic drawing of the N-terminal (a) and the C-terminal (b) part of the model representing the partly helical chain, with three linked peptide units at each end (C$^\alpha_{-3}$ to C$^\alpha_0$ and C$^\alpha_j$ to C$_{j+3}$) belonging to the coil sequences. The residues 0, 1, 2, ... and $j - 2$, $j - 1$, j, for which the dihedral angles ϕ and ψ are fixed, belong to the helical sequence. The hydrogen bonds are represented by heavy broken lines.

II. Description of the Model

The model representing the partly helical polypeptide chain is shown in Figure 1. It is composed of two parts corresponding to the N-terminal end (Figure 1a) and the C-terminal end (Figure 1b) of the chain.

Each of the coil sequences comprises three linked peptide units. All the interior C$^\alpha$ atoms except C$^\alpha_{-2}$ and C$^\alpha_{-1}$ at the N-terminal end and C$^\alpha_{j+1}$ and C$^\alpha_{j+2}$ at the C-terminal end are fixed in a α helical conformation. The dihedral angles ϕ_{-2}, ψ_{-2}, ϕ_{-1}, ψ_{-1} (Figure 1a) and ϕ_{j+1}, ψ_{j+1}, ϕ_{j+2}, ψ_{j+2} (Figure 1b) for rotation around the skeletal bonds formed by the C$^\alpha_{-2}$, C$^\alpha_{-1}$, C$^\alpha_{j-1}$, and C$_{j+1}$ atoms are free to assume any value in the allowed region of the steric map of the corresponding residue. In both parts (a) and (b) of the model, nine C$^\alpha$ atoms are confined to a helical conformation, thus representing 2.5 turns of a helix.

A standard geometry has been assumed for the polypeptide chain, and the interactions between atoms have been represented by a hard-sphere potential. The radii of atoms were taken from Knaell and Scott,[7] but the radius of the carbon atom was slightly diminished (by 0.05 Å) so that the potential was somewhat softer.

In order to take account of hydrogen bond formation, the oxygen and hydrogen on nitrogen were allowed to approach each other as close as 1.35 Å and oxygen and nitrogen as close as 2.35 Å. According to Poland and Scheraga,[8] the repulsion between these atoms at such a distance amounts to several kilocalories.

The conformational states in the coil sequence have been chosen in the allowed region of ϕ,ψ steric map of the corresponding residue by varying each of the rotational angles in steps of 30°. The total number of conformational states was 23 for the L-alanyl residue and 74 for the glycyl residue. The ratio of the number of allowed states 3.2 is equal

to the ratio of the surfaces of the allowed regions of the two steric maps.

In the helical sequence, ϕ and ψ have been fixed at −48 and −57°. This α helical state corresponds to a standard geometry of the polypeptide chain.[7] The parameters h and t of the resulting helix are 1.492 Å and 99.02°, and the $r_{O\cdots H}$ distance is equal to 1.84 Å. Because this α helical state is to be included into the set of conformational states of a residue in the coil sequence, the values of ϕ and ψ of other common regular structures[9] have also been introduced into the set, instead of the nearest round value of ϕ and ψ. Although such a choice of conformational states may mean weighting differently some of the points, it has the advantage of giving results very similar to those obtained with a larger set of states, derived from a conformational map by varying the rotational angles in steps of 20°, as it has indeed been verified in a few typical cases.

The calculations have been performed on the CDC 6400 electronic computer by examining the distances between all atoms and rejecting those conformations where at least one short contact appeared.

III. Determination of σ

Let us consider the partition function Z_γ corresponding to the distribution of the chain as described above, with i and j residues in coil and helical sequences respectively. Z_γ is given by the following expression

$$Z_\gamma = \left(\frac{2\pi}{l}\right)^{2i} f_i b^j \exp[-(j-2)e_H/RT] \qquad (7)$$

Equation 7 can be obtained from (6) by replacing the integration over the i degrees of freedom of the residues in coil sequences by a summation; l is the number of points into which the interval for each dihedral angle is divided for the numerical evaluation, f_i represents the total number of allowed conformations for the chain, and e_H is the energy per mole of the hydrogen bonds of which $(j-2)$ occur in a finite helical sequence of j residues.

Furthermore it has been assumed that the dihedral angles ϕ,ψ for each residue in the helical sequence are confined to a small region of conformational space of surface b.

Consequently we have the following expression for v_0

$$v_0 = b \exp[-e_H/RT] \qquad (8)$$

Using (7) and (8) we obtain from eq 3

$$\sigma = \frac{Z_\gamma}{u_0{}^i b^j \exp[-je_H/RT]} = \frac{\left(\frac{2\pi}{l}\right)^{2i} f_i \exp[2e_H/RT]}{u_0{}^i} \qquad (9)$$

For u_0 we can use the partition function z of a residue, computed from the corresponding steric map,[10] considering that for a random-coil polypeptide chain we have in a first approximation $u_n = z^n$.

When the conformational energy $E(\phi,\psi)$ of a residue is represented by a hard-sphere potential, we have, according to the above approximation

$$u_0 = \int_0^{2\pi} d\phi \int_0^{2\pi} d\psi \exp[-E(\phi,\psi)/RT] = (4\pi^2/l^2) f_0 \qquad (10)$$

where f_0 is the number of allowed states in the steric map among the l^2 states considered in the summation.

For the present case, with $l = 12$, we obtain

$$u_0{}^{Ala} = \left(\frac{4\pi^2}{144}\right) 23$$

and (11)

$$u_0{}^{Gly} = \left(\frac{4\pi^2}{144}\right) 74$$

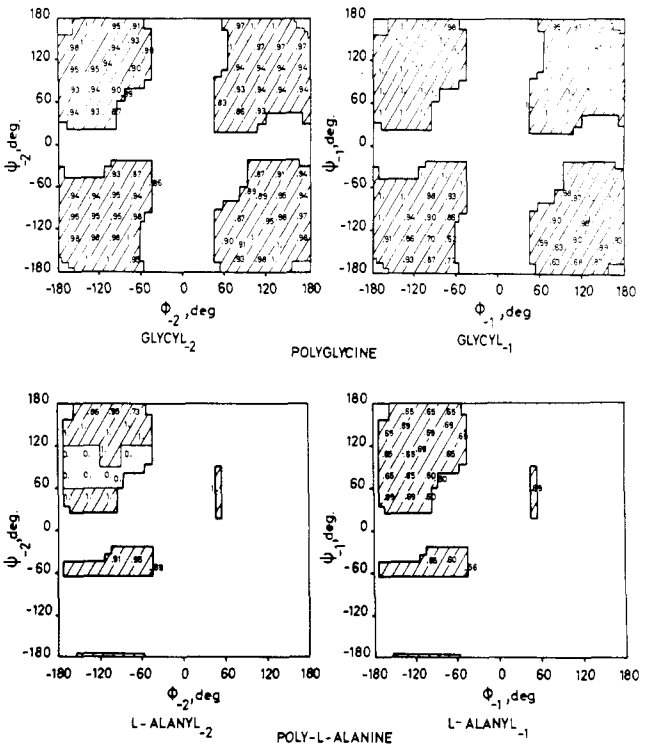

Figure 2. Steric maps for the residues −2 and −1 at the N-terminal end of the helix in polyglycine and poly(L-alanine), showing the states which are not excluded (hachured area) and the number of allowed conformations of the chain for each pair of dihedral angles ϕ_{-2},ψ_{-2} and ϕ_{-1},ψ_{-1}, expressed as a fraction of the corresponding member in an unattached system of three linked peptide units. The outer contours represent the sterically allowed states for a residue in a dipeptide unit.

for L-alanyl and glycyl residues.

In order to obtain the numerical value of σ as given by eq 9, the only quantities which have to be computed are f_i and u_0.

IV. Numerical Results

A. Homopolymers. In Figures 2 and 3 we have represented at every point of ϕ,ψ space of each residue k in the coil sequence at the N-terminal end and the C-terminal end of the helix in polyglycine and poly(L-alanine) the number of allowed conformations of the chain for this value of ϕ_k,ψ_k, expressed as a fraction of the corresponding number f_0 of states in an unattached system of three linked peptide units.

This number, defined by eq 10, is equal to 23 and 74 for three linked peptide units Ala·Ala and Gly·Gly, respectively.

The ratio of the total number of allowed states in the coil sequence at the N-terminal end to the total number of allowed states in an unattached system of three linked peptide units, $f_0{}^i$ $(i = 2)$, is 0.66 for poly(L-alanine) and 0.95 for polyglycine. At the C-terminal end, 0.22 and 0.59 of the total number of $f_0{}^i$ states available for an unattached coil sequence are allowed for poly(L-alanine) and polyglycine, respectively.

The reason for this difference between the two polypeptides is apparent from Figure 3. Almost all of the conformational space in the interval of ϕ_{j+1} between −180 and 0° is disallowed for the first residue in the coil sequence, for both poly(L-alanine) and polyglycine, while the second half of the conformational space, in the interval of ϕ_{j+1} between 0 and +180°, is free of steric constraints. However, for L-alanyl residue this part of conformational space is disal-

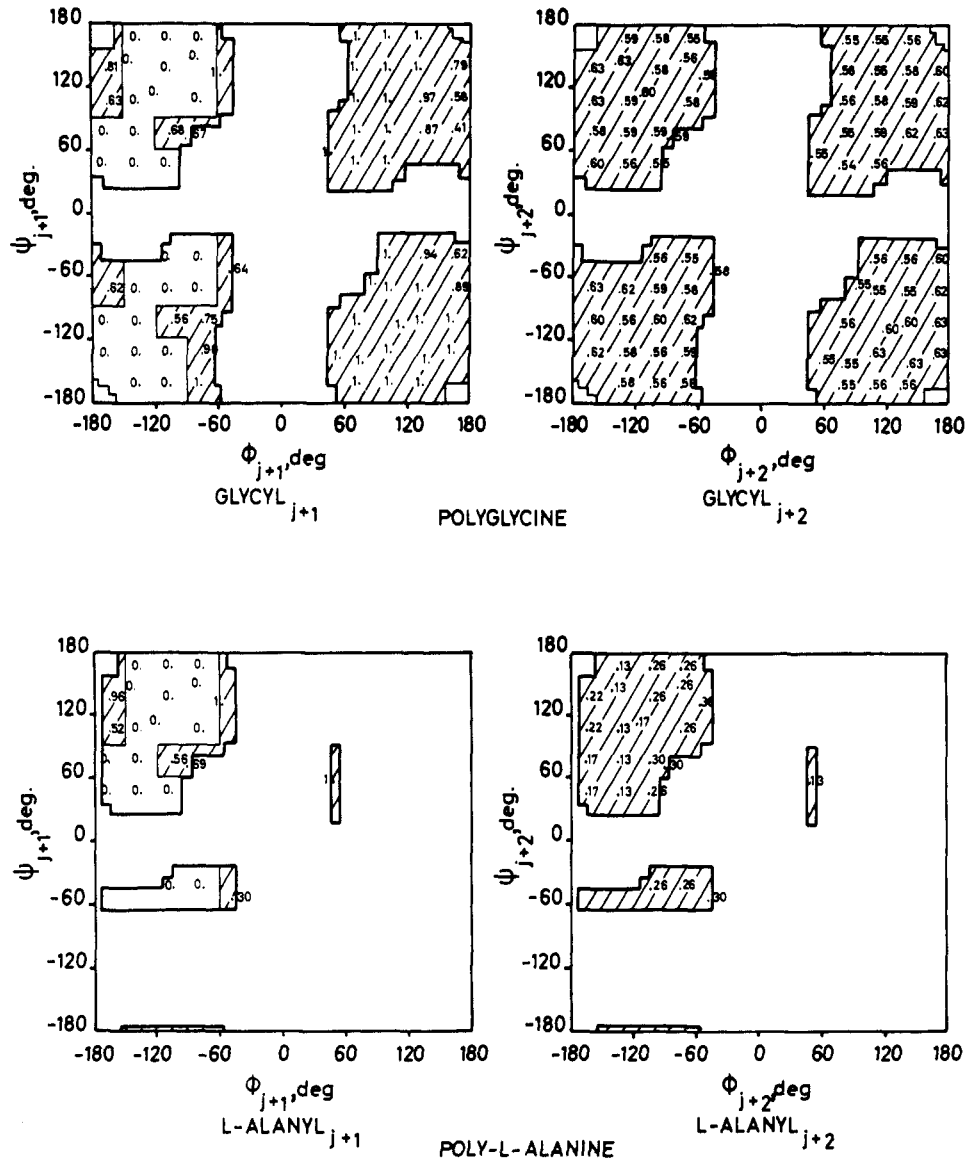

Figure 3. Steric maps for the residues $j + 1$ and $j + 2$ at the C-terminal end of the helix in polyglycine and poly(L-alanine), showing the states which are not excluded (hachured area) and the number of allowed conformations of the chain for each pair of dihedral angles ϕ_{j+1},ψ_{j+1} and ϕ_{j+2},ψ_{j+2}, expressed as a fraction of the corresponding number in an unattached system of three linked peptide units. The outer contours represent the sterically allowed states for a residue in a dipeptide unit.

lowed because of steric conflicts among the atoms of the free unit itself. Consequently there is a much greater relative reduction in the number of allowed states for poly(L-alanine) than for polyglycine.

The short contacts responsible for the exclusion of the left-hand side of the conformational map of residue $j + 1$ involve mainly the atoms of the peptide bond $(CO)_{j+1}$–$(NH)_{j+2}$ and the unbonded oxygen O_{j-2} in the helical sequence. These steric repulsions are due to the orientation of the oxygen atom, which extends in the direction of the coil sequence, and to the proximity in space of the oxygen O_{j-2} and of peptide bond. Some of the excluded conformations would lead to a hydrogen bond as in a regular helix, but in all cases the number of these conformations is less than 3%, so that it is not essential to exclude these conformations from the statistical weight of the coil sequence.

At the N-terminal end, the bulky oxygen atoms extend in the direction opposite to that of the coil sequence. Here the number of disallowed states is less. In poly(L-alanine), most of the short contacts involve methyl groups of the residue 1 adjoining the helix and the methyl of the $C^{\alpha}{}_2$ atom in the helical sequence (Figure 1b). Using eq 9 and 11 we obtain, from the number of allowed states quoted above, the following values

$$\sigma_{Ala} = 0.15 \exp[2e_H/RT]$$

$$\sigma_{Gly} = 0.56 \exp[2e_H/RT]$$

for poly(L-alanine) and polyglycine, respectively. Due to the flexibility of glycine, the effect of the longer range interactions between the coil and helical section on σ is much less for the glycine than for the alanine polypeptide. The absolute value of σ depends of course on the value of e_H in both peptides.

B. Copolymers. In Table I are shown four relative values of σ which can be obtained for a sequential polypeptide $(Ala\text{-}Gly)_x$ assuming that e_H has a constant value. Such sequential polypeptides have been investigated experimentally.[11]

At the C-terminal end, the atoms of the side chain of the amino acid in the helical section are not involved in short contacts. At the N-terminal end, the steric contacts depend

Table I
Values of σ Determined by (9) for a Sequential Polypeptide (Ala·Gly)$_x$

Composition of the coil sequence		σ exp-[$-2e_H/RT$]
N-terminal end	C-terminal end	
Gly·Ala	Gly·Ala	0.54
Ala·Gly	Gly·Ala	0.39
Gly·Ala	Ala·Gly	0.23
Ala·Gly	Ala·Gly	0.16

on the type of the side chain of the third residue in the helical section (C^{α}_2, Figure 1b).

As it is seen from Table I, the value of σ for (Ala·Gly)$_x$ is almost identical with that of polyglycine when the composition at the N-terminal and C-terminal end is Gly·Ala. This result shows that for the present model the value of σ is determined essentially by the steric interactions between the first residue in the coil sequence at the C-terminal end of the helix and the latter. Of course this conclusion is only valid in case e_H is independent of the composition.

We have also investigated how the partition function Z_γ (eq 7) of a chain of poly(L-alanine) is affected when a glycyl residue is incorporated into the coil sequence at the C-terminal end of the chain. As the model used for the partition function of a peptide chain in completely helical conformation is independent of the composition, the logarithm of the numbers given in the third column of Table II is equal, apart from a constant term, to the change in free energy on going from completely to partly helical conformations. This free energy change is particularly large in chains where there is a glycyl residue at the junction of the helical and coil sequences at the C-terminal end.

It should be kept in mind that in the present model all the differences between the interactions of the side chains, except the steric ones, are being neglected. Therefore the values given in Tables I and II are representative only for the steric factors.

V. Discussion

The main advantage to define σ by eq 3 as compared with the definition of ref 4 is that the artificial separation of the chain in helical and coil sequences is avoided. Instead, σ is obtained naturally from the numerically determined partition function of the whole chain with a given distribution in helical and coil sequences and will represent therefore the contribution from modified energy and entropy at the ends of helical as well as coil sequences. It appears moreover from the numerical evaluation of σ that the entropy of the residues at the ends of coil sequences is considerably reduced. The reduction of entropy is more important in poly(L-alanine) than in polyglycine because of the flexibility of the glycyl residue.

The length of the coil section, which was limited here to only two residues, seems to be long enough for the determination of σ, because the largest contribution to σ is due to steric repulsions between the helix and the first peptide unit in the coil sequence.

However, in the present numerical evaluation of σ, many assumptions have been made which may be avoided in more elaborate calculation. These are: (a) the use of hard-sphere potential for representing the interatomic forces; (b) the definition of u_0 by eq 10 and thus neglecting interactions between dipeptide units; (c) the neglect of the difference in the phase space volume b for a residue in a helical sequence bound by two and by one hydrogen bond; (d) only regular helices have been considered.

Table II
The Partition Function Z_γ for the Model of Poly(L-alanine) with 0, 1, and 2 Glycyl Residues in the Coil Sequence at the C-Terminal End of the Helix

Composition of the coil sequence		$Z_\gamma \exp[-2e_H/RT] \times 10^{-3}$
N-terminal end	C-terminal end	
Ala·Ala	Ala·Ala	0.23
Ala·Ala	Ala·Gly	0.78
Ala·Ala	Gly·Ala	1.80
Ala·Ala	Gly·Gly	6.21

Among the above assumptions, we feel that only (a) and (d) may have significant consequence on the numerical value of σ. In particular, the values for σ_{Gly} and σ_{Ala} may decrease for helices with modified angles ϕ and ψ at their ends. Such helices cannot be described without introducing explicitly a hydrogen bond potential and an interatomic potential composed of a repulsive as well as of an attractive part. Such a model will be reported later and comparison with experimental data will then be considered.

The conclusions obtained from the present numerical evaluation of σ are therefore limited, mainly because of the approximations inherent to the hard-sphere model.

In particular the enthalpic contribution both to σ and s is not taken into account properly. For instance, the parameter s, as obtained from eq 8 and 10, is given by the expression

$$s = b \exp(-e_H/RT)/(2\pi/l)^2 f_0 \qquad (12)$$

where e_H is to be understood as the hydrogen bond energy, independent in the side chain of the residues in the helical sequence.

The parameter σ as well arises from purely entropic contributions. This is clearly seen from a comparison of σ as deduced from the Zimm and Bragg[2] definition of a helical sequence, σ_{ZB}, with the value of σ deduced from the present definition, which is that of Lifson and Roig.[12] In the Zimm and Bragg definition a residue is helical when its CO or NH group is involved in a hydrogen bond.

We have therefore

$$\sigma_{ZB} = \sigma s^2 \qquad (13)$$

Replacing σ and s by their values as given by eq 9 and 13, we obtain

$$\sigma_{ZB} = (2\pi/l)^{2i} f_i b^2 / u_0^{(i+2)} \qquad (14)$$

which is indeed purely entropic.[13]

Nevertheless, the present hard-sphere model shows the importance of interactions between atoms in coil sequence with deeper atoms in an adjoining helical sequence in determining the value of σ.

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Solution Viscosities and Unperturbed Dimensions of Poly(vinylidene chloride)[1]

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ABSTRACT: Light-scattering molecular weights and dilute-solution viscosities have been measured for a series of unfractionated homopolymers of vinylidene chloride in tetramethylene sulfoxide and in *N*-methylpyrrolidone. From these results the characteristic ratio is estimated to be $C_\infty = 8 \pm 1$, which is somewhat larger than the accurately known value of 6.6 for poly(isobutylene). The larger value for poly(vinylidene chloride) can be rationalized as largely due to electrostatic dipole interactions.

Poly(vinylidene chloride) (PVDC) has long been an important commercial material,[2] but knowledge of its chain conformational properties is still relatively slight. The exact crystal structure is not yet settled,[2-4] and determinations of chain dimensions in solution have previously been published only for several copolymers of vinylidene chloride.[5,6] The lack of solution data is fundamentally due to the high crystalline melting point of the polymer (202°) which severely limits solubility at room temperature, and to thermal instability which prevents accurate work at higher temperatures. Recently, however, a wide search by Wessling[7] has revealed the existence of several solvents suitable for solution study of the homopolymer at ordinary temperatures. Here we report on light-scattering and viscosity measurements of a series of unfractionated samples of PVDC in several of Wessling's solvents, and from the results we estimate the unperturbed chain dimensions.

Apparently the only polymer of the structural type $(-CH_2CR_2-)_x$ for which conformational properties are well known at present is poly(isobutylene) (PIB), and it is clearly worthwhile to study at least one more member of this class. Furthermore, the relatively small difference between the van der Waals radii of the methyl group and the chlorine atom suggests that differences in conformational behavior between PVDC and PIB might be attributed in considerable part to the electrostatic dipolar interactions present in the former polymer. We have made calculations which lend some support to this suggestion.

Experimental Section

Vinylidene chloride (Polysciences, Inc.) was distilled over anhydrous magnesium sulfate. Polymerizations were effected with benzoyl peroxide initiator (1.5 mol % on monomer) at 60° in the presence of varying amounts of carbon tetrachloride as diluent and transfer agent. The customary freeze–pump–thaw cycle was used. Polymerization in sealed tubes was allowed to proceed for several days, after which the solid polymer was rinsed thoroughly with methanol before drying under vacuum to constant weight.

Tetramethylene sulfoxide, TMSO (Aldrich, bp 60–61° (0.3 mm)), and 1-methyl-2-pyrrolidone, MP (Eastman Kodak, bp 68° (8 mm)), were distilled under reduced pressure before use. Hexamethylphosphoramide, HMPA (Aldrich), was used for viscosity measurements as obtained. Solution viscosities were determined in Ubbelohde dilution viscometers at 25° in a bath controlled to ±0.02°. A Brice-Phoenix Differential Refractometer, Model BP-1000V, was used to obtain refractive-index increments, dn/dc, for PVDC of 0.0494 (±0.0004) $cm^3\ g^{-1}$ in TMSO and 0.0799 (±0.0004) in MP at a wavelength of 546 nm. Light-scattering intensities of PVDC solutions in TMSO and MP were measured at room temperature for unpolarized incident light (546 nm) with a Brice-Phoenix Model 1000 Light Scattering Photometer.

Usually it was necessary to warm the polymer–solvent mixtures to about 50 or 60° for 3 to 4 min in order to produce homogeneous solutions, but these could then be kept at room temperature without phase separation for at least some hours, quite long enough for the measurements. Absence of significant polymer degradation during the dissolution period was inferred from the fact that solutions raised to 70° for more than 5 min and then returned to 25° displayed negligible changes in solution viscosity. The MP solutions as measured usually were visibly very faintly yellow in color, but deliberate slight enhancement of this color by warming for short periods of time did not change the measured light scattering intensity, and no correction for absorption was applied. The TMSO solutions were colorless.

The preliminary light-scattering results reported earlier[8] have now been superseded by later measurements in which greater photometer sensitivity was achieved, in part by sacrificing angular resolution. Molecular weights were obtained by linear extrapolation based on the customary relation

$$Kc/R_{90} = (P_{90}M_w)^{-1} + 2A_2c + \ldots \qquad (1)$$

Corrections for depolarization of the scattered light were negligible. The molecular weights (all below 130×10^3) are too small for accurate measurement of angular dissymmetry, so the intramolecular scattering factors P_{90} were estimated as elsewhere[9,10] from the intrinsic viscosities. The figures reported in Table I are obtained as averages of the results obtained in the two solvents MP and TMSO. Second virial coefficients are not given for the lower molecular weights because of insufficient precision; for the two highest, the value of A_2 is 1.5×10^{-4} $cm^3\ mol\ g^{-2}$, which is close to that expected on the basis of the standard two-parameter correlation.[11]

Results

The weight-average molecular weights M_w and intrinsic viscosities $[\eta]$ obtained for the various samples in both TMSO and MP are shown in Table I. The estimated angular scattering factors $1/P_{90}$ alter the molecular weights by 4% at most. The table also includes intrinsic viscosities in HMPA, although with this solvent we could not prevent